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(54) CHEMICAL COMPOSITIONS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to tufted carpets and to adheisve compositions of use in the manufacture thereof and is particularly concerned with an improvement in or modification of the invention described and claimed in Patent Specification No. 1,205,460.

In preparing carpets for floor covering and similar uses it has been the practice to apply adhesives as backsizes in the form of a latex. The wet latex is spread onto the backside of the carpet and is then dried or cured by heating. The use of a latex is both time consuming and requires careful control in order to prevent damage to the tufted structure. On the other hand, the use of hot melt polymeric adhesives is also frequently accompanied by disadvantages. Such disadvantages are usually found in one or more of the following characteristics: insufficient strength properties involving both the toughness of the adhesive itself and its adhesive strength in bonding to other carpet materials, improper melt viscosity at the temperatures at which application to the carpet is to be accomplished, poor hand of the finished carpet, and a low adhesive softening point.

The toughness of an adhesive composition is defined as the product of its tensile strength at yield (lbs./in.^{2}) and its percent elongation at break. These properties are measured on a cast film of the composition using an Instron (registered Trade Mark) tester. A toughness of at least 11,000 is usually considered acceptable. Aside from toughness, the other strength property of a backsizing composition is its adhesive strength. This property is generally indicated by the carpet's pill or fuzz resistance and secondary backing bond. Pill resistance is measured by tumbling carpet samples in the presence of an abrading material for ten hours and subsequently visually rating the development of pilling using a rating scale of 1 to 5. A value of 4 or better is considered acceptable. The secondary backing bond is meaningful when an addditional backing material is applied to the tufted carpet after the adhesive application. This bond is measured by basic peel test techniques on 3 inch wide strips. A value of 10 lbs./3 in. is considered the minimum acceptable value.

Except for very heat sensitive fibers, the adhesive application to the carpet is generally accomplished at a temperautre of about 220°F.—340°F. Consequently, viscosity measurements are made over this temperature range and a desirable adhesive composition should have a Brookfield viscosity (spindle #7; 50 r.p.m.) of about 1,000 centipoises—

15,000 centipoises within the aforementioned temperature range. When using compositions with appreciably higher viscosities, difficulty is encountered in getting adhesive penetration into the fibers. At lower viscosities excessive penetration is observed and, if a secondary backing material is to be applied, it is difficult to achieve proper adhesion.

For commercial acceptance a finished carpet must have a suitable feel which is customarily referred to as carpet "hand". Good carpet "hand" is associated with a feeling of stiffness or body. The rigidity of the adhesive composition, as reflected by the elastic modulus, influences the carpet's "hand"; particularly when the adhesive composition does not contain filler and low coating weights are used. In such instances, compositions with an elastic modulus of 5,000—20,000 psi, preferably 8,000—17,000 psi, are suitable. As higher coating weights or filled compositions are employed, the modulus of the composition diminishes in significance with respect to influencing carpet "hand".

The adhesive composition's softening point is related to the temperature at which the adhesive bond in the backsized carpet fails. This temperature is indicated by the ring and ball softening point (ASTM E—28—58T) of the adhesive composition which should be at least 190°F. A carpet backsized with such adhesives can withstand commercial cleaning techniques and can be used on floors subjected to high temperatures such as those wherein radiant heating is employed. Furthermore, such carpets can also be stored and shipped under conditions of elevated temperatures.

Patent Specification No. 1,205,460 describes and claims an adhesive composition having a softening point of at least 190°F., which comprises (A) 10—35 weight percent ethylene copolymer having a melt index of 1.2—35 and comprising 60—85 weight percent copolymerized ethylene and 15—40 weight percent copolymerized lower vinyl ester (as therein defined), lower acrylate (as therein defined) or lower methacrylate (as therein defined), (B) 10—25 weight percent of a wax having a melting point sufficiently high to provide the composition with a softening point of at least 190°F, and (C) 50—70 weight percent blend of (a) an aliphatic thermoplastic hydrocarbon resin substantially free of polymerized aromatics prepared from an olefin monomer and a diene each containing 5 to 7 carbon atoms and having a softening point of 155°F.—240°F. and (b) a dicyclopentadiene alkylation polymer resin having a softening point of 40°F.—105°F.; the weight percentages of (A), (B), and (C) being based on the combined weight of these three ingredients and the weight ratio of (a) to (b) being 0.3—1.5.

According to one feature of the present invention there is provided an adhesive composition having a softening point of at least 190°F., which comprises (A) 10—35 weight percent ethylene copolymer having a melt index of 1.2—35 and comprising 60—85 weight percent copolymerized ethylene and 15—40 weight percent copolymerized lower vinyl ester (as herein defined), lower acrylate (as herein defined), or lower methacrylate (as herein defined), (B) 10—25 weight percent of a wax having a melting point sufficiently high to provide the composition with a softening point of at least 190°F, and (C) 50—70 weight percent blend of (a) an aliphatic thermoplastic hydrocarbon resin substantially free of polymerized aromatics prepared from an olefin monomer and a diene each containing from 5 to 7 carbon atoms and having a softening point of 155°F.—240°F. and (b) a dicyclopentadiene alkylation polymer resin having a softening point of 40°F.—105°F.; the weight percentages of (A), (B), and (C) being based on the combined weight of these three ingredients and the weight ratio of (a) to (b) being at least 1.5, preferably 1.5 to 4.0.

According to a further feature of the present invention there is provided a carpet having a primary backing material stitched with closely spaced erect loops of yarn to form a tufted structure, the bottom surface of the tufted structure including, as an adhesive coating, a composition according to the invention as hereinbefore defined.

In application, the composition according to the invention in a molten state may, for example, be distributed substantially uniformly across the backside of a tufted carpet which has carpet yarn stitched to a backing material and, thereafter, the adhesive solidified by cooling. Also, the present adhesive is particularly suitable when it is desirable to apply a secondary backing material to the carpet. The secondary backing material may be applied almost immediately after the adhesive application to the carpet backside; there being no necessity for an intermediate cooling or drying step. Of course, the present adhesive may be used in preparing carpet containing no secondary backing material.

The manner in which the carpet is prepared prior to the adhesive application of the present invention is not particularly limited. The art of preparing tufted carpets is well known and generally comprises stitching a primary backing material with yarn in such a manner as to form on the top surface of the material a pile composed of numerous closely spaced erect loops of yarn. The yarn at the base of each loop extends through the primary backing and is visible on the bottom surface of the resulting loop-stitched or "tufted" structure. The adhesive composition of the present invention is applied to the bottom surface of the tufted structure and, consequently, the bottom of the primary backing material and the base portion of the loops of pile yarn are coated with the adhesive composition.

As with the method of preparing the tufted carpet prior to the adhesive application of the present invention, any of a wide variety of known yarns and backing materials, including both synthetic and natural materials, can be used in the present invention. For a detailed description of methods and materials useful in making tufted carpets, prior to the particular adhesive application of the present invention, reference is made to Seymour Sands' United States Patent 3,390,035.

Similarly, any method known in the art of applying coatings of molten thermoplastic adhesives can be employed for applying the adhesive composition in the present invention. For example, application techniques, such as extrusion, heated doctor blades, or passing the bottom surface of the tufted material in contact with the top surface of a rotating roller partially submerged in a tank of the molten adhesive, are suitable in the present invention. In general, the adhesive is applied in an amount equal to 10—25 ounces per square yard of the tufted material which, incidentally, is generally lower than that required with latex formulations.

Also, the adhesive of the present invention is suitable for use on carpets when it is desirable to apply a secondary backing to the adhesively bonded tufted carpet. As previously emphasized, a particular advantage of the present adhesive is that the secondary backing can be applied without the necessity of drying the adhesive. Of course, if desired, the adhesive can be solidified prior to application of the secondary backing and subsequently reactivated by simply heating the exposed surface until it is in a molten state. Useful secondary backing materials are well known and include those used as primary backing materials.

The particular adhesive composition of the present invention contains the following three essential ingredients: an ethylene copolymer, a wax component, and a resin extender blend of a base resin and a modifying resin. As hereinafter set forth, the composition of the present invention consists essentially of the three named ingredients in particular proportions. However, other ingredients, which do not basically detract from the compostiion's adhesive characteristics, can also be included. In fact, a filler material is frequently present while ingredients, such as antioxidants, pigments and plasticizers, among others, can also be included.

The ethylene/lower vinyl ester copolymers used in the present invention are ethylene copolymers with lower vinyl esters of carboxylic acids containing up to 5 carbon atoms. Such ethylene/lower vinyl ester copolymers can be prepared by known techniques, such as illustrated in U.S. Patent 2,200,429 and U.S. Patent 2,703,794. While an ethylene/vinyl acetate copolymer is preferred, other ethylene copolymers, such as those of vinyl formate, vinyl propionate, and vinyl butyrate, are useful as well. Additionally, ethylene copolymers of lower acrylates and lower methacrylates, these esters being derived from acrylic or methacrylic acid respectively and an alcohol containing up to 5 carbon atoms, may also be used. Examples of suitable lower acrylates and methacrylates include compounds such as beta-dimethylaminoethyl methacrylate, beta-hydroxyethyl acrylate, ethylene glycol dimethacrylate and isobutyl acrylate. The ethylene copolymers have melt indexes, as measured by ASTM 1238—52T, of 1.2—35, preferably 1.6—20, with a copolymerized ethylene content of 60—35 weight percent and preferably 72—82 weight percent. Correspondingly, the polymerized ester content of useful ethylene copolymers is between 40—15 weight percent, and preferably 28—18 weight percent. Additionally, ethylene copolymers containing minor amounts (i.e., up to 3 weight percent) of other polymerizable comonomers, such as acrylic acid, methacrylic acid, itaconic acid, acrylamide, diallyl maleate, diallyl phthalate or diallyl ether are useful as well.

Regarding the second essential ingredient in the present composition, i.e., the wax component, it is necessary that it have a melting point sufficiently high to give adhesive compositions with a softening point of greater than 190°F. Accordingly, the wax component can be either solely a Fischer-Tropsch wax or blends of high melting point petroleum waxes and low molecular weight polyolefin waxes wherein the polyolefin wax is at least 15 weight percent of the wax blend. The preferred high melting point petroleum waxes are those customarily known as microcrystalline waxes which have melting points in excess of 165°F. or paraffin waxes having melting points in excess of 140°F. Preferred low molecular weight polyolefin waxes are polyethylene waxes having a molecular weight of less than about 5,000 and melting points of 220°F.—250°F.

The third essential ingredient in the present adhesive composition is a unique resin extender blend of a base resin and a modifying resin. It has been discovered that the use of this blend in an ethylene copolymer-wax composition produces an adhesive backsizing composition with extraordinarily high toughness. Useful base resins are aliphatic thermoplastic petroleum hydrocarbon resins such as described in Canadaian Patent 531,202 issued October 2, 1956 to Ward. As therein set forth, the resins are prepared from reactive olefins and diene monomers containing from 5 to 7 carbon atoms, and are substantially free of polymerized aromatics. Of the resins therein described, those having molecular weights of about 800—1750, iodine numbers of 40—66, and ring and ball softening points (ASTM D—36—26) of 155°F.—240°F., and especi-

ally above 215°F., are preferred. Such useful base resins are available under the registered Trade Mark " Piccopale " of the Pennsylvania Industrial Chemical Corporation.

Modifying resins useful in the present invention are low molecular weight dicyclopentadiene alkylation polymers having ring and ball softening points of about 40°F.—105°F. Dicyclopentadiene alkylation polymers are described in U.S. Patent 3,023,200 issued February 27, 1962 to Epstein and Gangemi. As therein defined, the term " alkylation " refers to the formation of a carbon to carbon bond between an aromatic nucleus and a dicyclopentadiene nucleus. Also, this patent describes how dicyclopentadiene alkylation polymers can be prepared with desired softening points and molecular weights. Particularly useful modifying resins have specific gravities of 0.90—1.1, melt viscosities of about 1 poise over the temperature range of 175°F.—265°F., and softening points of 65°F.—90°F.

The weight ratio of base resin to modifying resin in compositions according to the present invention is advantageously 1.5—4.0. At substantially higher ratios the resulting adhesive compositions is brittle and is thus not preferred for use in carpeting application. The use of lower weight ratios is in accordance with Patent Specification No. 1,205,460.

The preferred ratio of base to modifying resin for a particular composition is selected so as to yield a finished carpet having an optimum " hand ", and in compositions according to the invention is preferably from 1.5 to 2.5. The compositions according to the invention preferably do not contain filler and are particularly useful in the application of low coating weight. If the wax component of the adhesive is predominantly a hard wax, such as paraffin, good " hand " can be obtained at lower ratios than if a soft wax is used.

The proportional amounts of the three essential ingredients in the adhesive composition is important. In general, the ethylene copolymer is present in an amount of 10—35 weight percent and preferably 12—25 weight percent, based on the total weight of the three ingredients. At lower copolymer contents, the adhesion and toughness characteristics of the blend are diminished while at higher copolymer contents the viscosity of the blend at application temperatures becomes too high. On the other hand, in order to avoid excessive brittleness, the wax ingredient is generally not present in amounts greater than 25 weight percent. However, at least about 10 weight percent wax is necessary in order to impart a high softening temperature to the composition. Correspondingly, the resin extender blend content is generally from 50—70 weight percent. The use of lower proportions of this ingredient tends to increase melt viscosity at application temperatures, while higher amounts diminish the adhesive's toughness. Preferably, the amount of resin extender blend and wax are 60—70 and 15—20 weight percent, respectively.

Where fillers are used in the compositions according to the invention, suitable fillers are well known; examples of which include clay, talc, calcium and magnesium silicates, calcium carbonate and wood flour. While filled compositions generally cost less per pound, it is necessary that they be employed at coating weights of 20—25 ounces per square yard. The compositions according to the invention are however preferably used unfilled at lower coating weights of 10—20 ounces. Filled compositions can if desired be prepared with filler contents up to 45 weight percent, based on the total composition.

The particular manner in which the ingredients are added to formulate the composition of the present invention is not critical and can be accomplished by any of the well known techniques. In general, the wax is initially melted, usually in the presence of an antioxidant, and thereafter the resin extenders are uniformly blended in. Subsequently, the ethylene copolymer, generally in a solid form, such as pellets, and fillers are blended into the wax/resin mixture.

The following Examples are given by way of illustration only and they show filled adhesive compositions of the present invention with all parts and percentages being by weight based on the total composition including antioxidant, unless otherwise indicated.

Example	A	B	C	D	E	F	G	H
Ethylene/Vinyl acetate copolymer (75 wt. % Et/25 wt. % VAc—M.I. 2)	10.0	10.0	15.0	15.0	21.4	21.4	21.4	21.4
Paraffin Wax(1)	None	None	None	None	14.6	14.6	14.6	14.6
Microcrystalling Wax (2)	11.1	11.1	10.2	10.2	None	None	None	None
Polyethylene Wax(3)	2.0	2.0	1.8	1.8	2.6	2.6	2.6	2.6
Modifying Resin(4)	18.0	9.4	17.1	14.3	20.4	17.5	15.3	12.2
Base Resin(5)	28.7	37.3	25.7	28.5	40.8	43.7	45.9	49.0
Filler ($CaCO_3$, average particle size 2.5μ)	30.0	30.0	30.0	30.0	None	None	None	None
"Tenox" BHT antioxidant ("Tenox" is a registered Trade Mark)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Elastic Modulus (psi)	4750	14,700	11,700	18,630	15,220	22,200	19,870	31,080

(1) Sinclair 153 wax (Melting point of 153°F.)

(2) Shell MX Wax 170 (Melting range 172—180°F.)

(3) "Polyethylene AC—8" — (Allied Chemical Corp. — Average molecular weight 3500; M.P. 240°F.)

(4) "Piccovar" AP—25—(Pennsylvania Industrial Chemical Corp.'s Dicyclopentadiene alkylation polymer, softening point 71°F.—83°F., specific gravity 0.97).

(5) "Piccopale" 110SF — (Pennsylvania Industrial Chemical Corp., softening point 225°F.—246°F., specific gravity 0.97).

Examples A—D have desirable application viscosities and the toughness and softening point of the blends of the three essential components in the formulations are above the minimum requirements. Furthermore, carpets backsized with these formulations display excellent pill resistance, secondary backing bond, and have good "hand".

EXAMPLE J

An even pile nylon carpet (22—24 oz. of face yarn/yd²) with jute primary backing was backsized with a $CaCO_3$ filled adhesive according to the invention at a coating weight of 18.8 oz/yard, a coating speed of 15 feet/min., and at a temperature of 275°F. Subsequent to the adhesive application, and prior to solidification, a secondary jute backing was applied. A second carpet was also coated with the same formulation as above except that the application temperature was raised to 280°F. and the coating weight lowered to 16.4 oz/yd.

The carpet samples were tested for pill resistance and secondary backing bond as previously described and they showed generally desirable properties.

As with the filled formulations, Examples E—H show good backsizing adhesive properties with respect to application viscosity, adhesive strength, and softening point. Carpets prepared with these compositions have good hand at low coating weights.

WHAT WE CLAIM IS:—

1. An adhesive composition having a softening point of at least 190°F., which comprises (A) 10—35 weight percent ethylene copolymer having a melt index of 1.2—35 and comprising 60—85 weight percent copolymerized ethylene and 15—40 weight percent copolymerized lower vinyl ester (as herein defined), lower acrylate (as herein defined), or lower methacrylate (as herein defined), (B) 10—25 weight percent of a wax having a melting point sufficiently high to provide the composition with a softening point of at least 190°F, and (C) 50—70 weight percent blend of (a) an aliphatic thermoplastic hydrocarbon resin substantially free of polymerized aromatics prepared from an olefin monomer and a diene each containing from 5 to 7 carbon atoms and having a softening point of 155°F—240°F. and (b) a dicyclopentadiene alkylation polymer resin having a softening point of 40°F.—105°F.; the weight percentages of (A), (B), and (C) being based on the combined weight of these ingredients and the weight ratio of (a) to (b) being at least 1.5.

2. A composition as claimed in claim 1 which contains from 12 to 25 weight percent of component A based on the combined weight of components A, B and C.

3. A composition as claimed in claim 1 or claim 2 in which the ethylene copolymer of component A has a melt index of from 1.6 to 20.

4. A composition as claimed in any of the preceding claims in which the ethylene copolymer of componet A contains from 72 to 82 weight percent of copolymerised ethylene.

5. A composition as claimed in any of the preceding claims in which the ethylene copolymer of component A contains from 18 to 28 weight percent of a copolymerised vinyl ester, acrylate or methacrylate.

6. A composition as claimed in claim 5 in which the said vinyl ester is vinyl acetate, vinyl formate, vinyl propionate or vinyl butyrate.

7. A composition as claimed in claim 5 in which the said acrylate is isobutyl acrylate.

8. A composition as claimed in any of the preceding claims which contains from 15 to 20 weight percent of component B based on the combined weight of components A, B and C.

9. A composition as claimed in any of the preceding claims in which the said high melting point wax comprises a Fischer-Tropsch wax.

10. A composition as claimed in any of the preceding claims wherein the major portion of the high melting point wax comprises a paraffin wax.

11. A composition as claimed in any of claims 1 to 10 in which the said high melting point wax comprises a blend of a high melting point petroleum wax and a low molecular weight of polyolefin wax.

12. A composition as claimed in claim 11 in which the said blend contains at least 15 weight percent of the low molecular weight polyolefin wax.

13. A composition as claimed in claim 11 or claim 12 in which the high melting point petroleum wax is microcrystalline and has a melting point greater than 165°F.

14. A composition as claimed in any of claims 11 to 13 in which the low molecular weight polyolefin wax is a polyethylene wax.

15. A composition as claimed in claim 14 in which the said polyethylene wax has a molecular weight of less than 5000.

16. A composition as claimed in claim 14 or claim 15 in which the polyethylene wax has a melting point of from 220 to 250°F.

17. A composition as claimed in any of the preceding claims which contains from 60 to 70 weight percent of component C based on the weight of components A, B and C.

18. A composition as claimed in any of the preceding claims in which the thermoplastic hydrocarbon resin has a molecular weight of from 800 to 1750.

19. A composition as claimed in any of the preceding claims in which the thermoplastic hydrocarbon resin has an iodine number of from 40 to 66.

20. A composition as claimed in any of the preceding claims in which the thermoplastic hydrocarbon resin has ring and ball softening point of from 155 to 240°F.

21. A composition as claimed in claim 20 in which the ring and ball softening point is above 215°F.

22. A composition as claimed in any of the preceding claims in which the alkylation polymer resin of component C has a specific gravity of from 0.90 to 1.1.

23. A composition as claimed in any of

the preceding claims in which the alkylation polymer resin of component C has a viscosity of about 1 poise when molten in the temperature range of from 175 to 265°F.

24. A composition as claimed in any of the preceding claims in which the alkylation polymer resin of component C has a softening point of from 65 to 90°F.

25. A composition as claimed in any of the preceding claims wherein the weight ratio of a) to b) is from 1.5 to 4.0, preferably 1.5 to 2.5.

26. A composition as claimed in any of the preceding claims which contains an antioxidant, pigment or plasticizer.

27. A composition as claimed in any of the preceding claims containing no filler.

28. A composition as claimed in any of the preceding claims in which the ethylene copolymer of component A containing up to 3 weight percent of units derived from copolymerizable monomers other than ethylene and the vinyl ester, acrylate or methacrylate.

29. A composition as claimed in claim 28 in which the said polymerizable monomer comprises acrylic acid, methacrylic acid, itaconic acid, acrylamide, diallyl maleate, diallyl phthalate or diallyl ether.

30. A composition as claimed in claim 1 substantially as herein described.

31. An adhesive composition substantially as herein described in any of the Examples.

32. A carpet having a primary backing material stitched with closely spaced erect loops of yarn to form a tufted structure, the bottom surface of the tufted structure including, as an adhesive coating, a composition as claimed in any of the preceding claims.

33. A carpet as claimed in claim 32 in which the adhesive composition is present at a coating weight of from 10 to 20 ounces per square yard.

34. A carpet as claimed in claim 32 which includes a secondary backing material.

35. A tufted carpet substantially as herein described in Example J.

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